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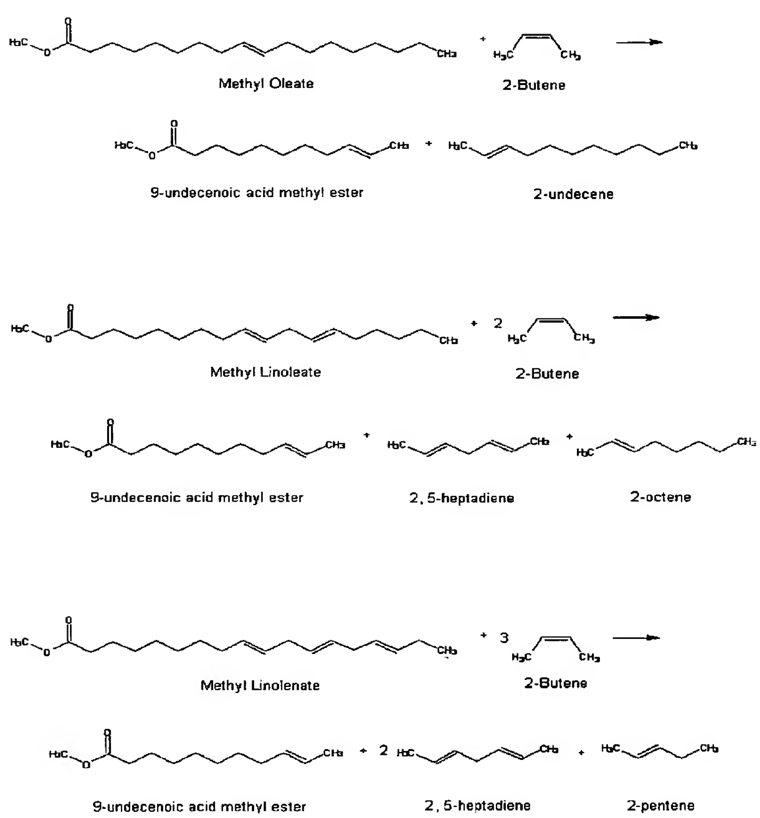


**(57) Abstract:** Described is a method of chemically modifying a starting composition comprising polyunsaturated alkene compounds in order to convert at least a portion of the polyunsaturated alkene compounds into functionalized monounsaturated alkene compounds. The separated monounsaturated alkene compounds may be useful, for example, as a starting material in the synthesis of organic chemicals such as diacids, diesters, and the like.

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# METHODS OF MAKING MONOUNSATURATED FUNCTIONALIZED ALKENE COMPOUNDS BY METATHESIS

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application having Serial No. 60/851,501, filed October 13, 2006, and entitled METHODS OF MAKING MONOUNSATURATED FUNCTIONALIZED ALKENE COMPOUNDS BY METATHESIS, the disclosure of which is incorporated herein by reference.

## GOVERNMENT RIGHTS

This invention was made with U.S. Government support under Award Number DE-FG36-04GO14016 awarded by the U.S. Department of Energy. The Government may have certain rights in this invention.

## BACKGROUND

Recently there has been an increased interest in using natural oils as feedstocks in the production of chemicals that historically have been produced from petroleum-derived feedstocks. In order to efficiently use natural oils as feedstocks, however, the isolation of a single organic compound that serves as the starting material for the synthesis is highly desirable. The isolation of a single organic compound from natural oils, which typically comprise a complex mixture of triglycerides (e.g., mixtures of mono, di, and triunsaturated C18 fatty acids), is difficult and expensive using conventional separation techniques.

One approach that can be taken is to chemically modify the natural oil in order to produce a modified composition that can be more readily separated to isolate a single organic compound. One known method for chemically modifying natural oils is through metathesis. Metathesis is a reaction that results in the chemical rearrangement of double-bond containing compounds. A schematic representation of a typical metathesis reaction is shown below.

$$R_1R_2C=CR_3R_4 + R_1R_2C=CR_3R_4 \rightarrow R_1R_2C=CR_1R_2 + R_3R_4C=CR_3R_4$$

When a natural oil comprising multiple species of saturated and unsaturated (including polyunsaturated) fatty acids is self-metathesized, the products include a mixture of monoacids, diacids, and olefins. Although this mixture may be more readily separated than the natural oil itself (e.g., due to the formation of low boiling olefin species), the boiling point separation in the metathesis products is not sufficient to allow convenient separation and isolation of single organic compound. For example, FIG. 1 depicts the predicted product mixture obtained by the self-metathesis of methyl soyate. As shown in FIG. 1, the various species present (i.e., olefins, methyl esters, and diesters) have similar and overlapping boiling point ranges, thus making separation difficult.

In view of the foregoing, what is needed is a method by which a natural oil can be chemically modified to facilitate the separation and isolation of a single organic compound or several closely related organic compounds.

## SUMMARY

The invention provides a method of chemically modifying a starting composition comprising functionalized polyunsaturated alkene compounds in order to convert at least a portion of the polyunsaturated alkene compounds into functionalized monounsaturated alkene compounds. In one aspect, the method of the invention comprises the steps of:

(a) providing a starting composition comprising one or more polyunsaturated fatty acids, polyunsaturated fatty esters, or carboxylate salts of polyunsaturated fatty acids;

(b) cross-metathesizing the starting composition with a short-chain olefin in the presence of a metathesis catalyst in order to form cross-metathesis products comprising: (i) one or more olefin compounds; and (ii) one or more functionalized monounsaturated alkenes; and

(c) separating at least a portion of one of the functionalized monofunctionalized alkenes from the cross-metathesis products to provide a functionalized monounsaturated alkene composition.

The method of the invention makes use of a cross-metathesis reaction with a short-chain olefin compound in order to chemically modify the starting composition. The chemical modification provides several advantages. First, the cross-metathesis

converts at least a portion of the polyunsaturated alkene compounds that are present in the starting composition into monounsaturated alkene compounds. In this way, the cross-metathesis product is enriched in monounsaturated alkene compounds as compared to the starting composition. Second, the cross-metathesis modifies the starting composition by creating two different classes of compounds in the cross-metathesis products. The two classes of compounds include: (1) functionalized monounsaturated alkene compounds, and (2) olefin compounds. Since the functionalized monounsaturated alkene compounds and the olefin compounds are different in molecular weight and polarity from one another, the functionalized monounsaturated alkene can be readily separated in order to provide a purified functionalized monounsaturated alkene compound. The separated functionalized monounsaturated alkene compounds may be useful, for example, as starting materials in the synthesis of organic chemicals such as diacids, diesters, and the like.

The effect of the cross-metathesis is shown in FIG. 2. FIG. 2 is a graph that displays the weight percent of cross-metathesis products (y-axis) against the estimated boiling point for the cross-metathesis products (x-axis) for a product mixture obtained from the cross-metathesis of methyl soyate with excess 3-hexene. As shown in FIG. 2, the monounsaturated ester product that is present at about 16% weight in the composition has a boiling point that is sufficiently separated from the remaining cross-metathesis products so that the monounsaturated ester can be isolated by conventional separation techniques.

Sources of polyunsaturated compounds to be used as the starting composition in the method of the invention include natural oils and animal fats. Representative examples of vegetable oils include soybean oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, sunflower oil, canola oil, safflower oil, palm oil, palm kernel oil, linseed oil, castor oil, olive oil, peanut oil, and mixtures thereof.

In many embodiments, the starting composition is an acid, ester, or salt functionalized polyunsaturated compound that can be represented by the general formula:

$$CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$$

where:

R is hydrogen, an aliphatic group, or a metal ion;

n1 is an integer equal to or greater than 0;

n2 is an integer equal to or greater than 0;

n3 is an integer equal to or greater than 0; and

x is an integer equal to or greater than 2.

In other embodiments, the starting composition is a polyunsaturated polyol ester that can be represented by the general formula:

$$R(O\text{-}Y)_m\,(OH)_n\,(O\text{-}X)_b$$

where

R is an organic group having a valency of (n+m+b);

m is an integer from 0 to (n+m+b-1), typically 0 to 2;

b is an integer from 1 to (n+m+b), typically 1 to 3;

n is an integer from 0 to (n+m+b-1), typically 0 to 2;

(n+m+b) is an integer that is 2 or greater;

X is $-(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$;

Y is $-(O)C\text{-}R'$;

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is an integer equal to or greater than 0;

n2 is an integer equal to or greater than 0;

n3 is an integer equal to or greater than 0; and

x is an integer equal to or greater than 2.

In yet other embodiments, the starting composition is a glyceride (i.e., a polyol ester of glycerol) that can be represented by the general formula:

$$CH_2A\text{-}CHB\text{-}CH_2C$$

where –A; –B; and –C are selected from

–OH;

$-O(O)C-(CH_2)_{n2}-[-CH=CH-(CH_2)_{n3}-]_x-(CH_2)_{n1}-CH_3$; and

$-O(O)C-R'$;

with the proviso that at least one of $-A$, $-B$, or $-C$ is

$-O(O)C-(CH_2)_{n2}-[-CH=CH-(CH_2)_{n3}-]_x-(CH_2)_{n1}-CH_3$.

In the above formula:

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is an integer equal to or greater than 0 (typically 0 to 15; more typically 0, 3, or 6);

n2 is an integer equal to or greater than 0 (typically 2 to 11; more typically 3, 4, 7, 9, or 11);

n3 is an integer equal to or greater than 0 (typically 0 to 6; more typically 1); and

x is an integer equal to or greater than 2 (typically 2 to 6, more typically 2 to 3).

In many embodiments, the starting composition comprises a Δ9 polyunsaturated fatty acid, a Δ9 polyunsaturated fatty ester, a carboxylate salt of a Δ9 polyunsaturated fatty acid, or a mixture thereof. Δ9 polyunsaturated compounds include a carbon-carbon double bond located between the 9th and 10th carbon atoms in the main chain of the fatty acid, ester, or salt. Examples of Δ9 polyunsaturated fatty acid include linoleic acid, linolenic acid, and mixture thereof. Examples of Δ9 polyunsaturated fatty ester include alkyl esters of linoleic acid, an alkyl esters of linolenic acid, or mixture thereof.

According to the method of the invention, the starting composition is cross-metathesized (see, step (b)) with a short-chain olefin in the presence of a metathesis catalyst. In many embodiments, the short-chain internal olefin is provided in stoichiometric excess relative to the starting composition. In some embodiments, the short-chain olefin has the structure:

$$R^7R^8C=CR^9R^{10}$$

where $R^7$, $R^8$, $R^9$, and $R^{10}$ are each, independently, hydrogen or an organic group, with the proviso that at least one of $R^7$ or $R^8$ is an organic group. In many

embodiments, the short-chain olefin is a short-chain internal olefin. For example, the short-chain internal olefin may have the structure:

$$R^7R^8C{=}CR^9R^{10}$$

where $R^7$, $R^8$, $R^9$, and $R^{10}$ are each, independently, hydrogen or an organic group, with the proviso that at least one of $R^7$ or $R^8$ is an organic group, and at least one of $R^9$ or $R^{10}$ is an organic group. Useful short-chain internal olefins may be symmetric or asymmetric. When symmetric, the short-chain internal olefin may have the structure:

$$R^7CH{=}CHR^9$$

where $R^7$ and $R^9$ are the same organic group. Examples of symmetric short-chain internal olefins include 2-butene, 3-hexene, and 4-octene. Examples of asymmetric short-chain internal olefin include2-pentene, 2-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 2-nonene, 3-nonene, and 4-nonene. In some embodiments, the short-chain olefin is an α-olefin having the structure:

$$CH_2{=}CH\text{-}R^{10}$$

where $-R^{10}$ is an organic group. Examples of α-olefin include 1-propene, 1-butene, 1-pentene, 1-hexene, 1-octene, and 1-nonene.

According to the method of the invention, after the cross-metathesis reaction, at least a portion of the monounsaturated functionalized alkene is separated from the other cross-metathesis products. Useful separation processes include distillation, reactive distillation, chromatography, fractional crystallization, membrane separation, liquid/liquid extraction, or a combination thereof. In many embodiments, the separated monounsaturated alkene composition is at least about 95% by weight pure, for example, at least about 96% weight pure, at least about 97% weight pure, at least about 98% weight pure, at least about 99% weight pure, or at least about 99.5% weight pure.

In many embodiments, the separated monounsaturated alkene composition has the structure:

$$R^7R^8C{=}CH\text{-}(CH_2)_{n2}\text{-}COOR$$

where R is hydrogen, an aliphatic group, or a metal ion;

n2 is an integer equal to or greater than 0; and

$R^7$ and $R^8$ are each, independently, hydrogen or an organic group.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph displaying the weight percentage and boiling points for certain self-metathesis products.

FIG. 2 is a graph displaying the weight percentage and boiling points for certain cross-metathesis products.

FIG. 3 is an exemplary reaction scheme for the method of the invention.

## DETAILED DESCRIPTION

The invention provides a method of chemically modifying a polyunsaturated alkene composition, such as a natural oil, in order to convert at least a portion of the polyunsaturated compounds that are present in the composition into monounsaturated alkene compounds, and in order to facilitate separation of the monounsaturated alkene compounds from the remaining cross-metathesis products.

The method of the invention may be found useful, for example, in modifying a starting composition that initially comprises one or more polyunsaturated fatty acids, fatty esters, or carboxylate salts of fatty acids in order to form a metathesized composition that comprises an increased amount of a monounsaturated alkene compound. Using conventional separation processes, the monounsaturated compound can be readily separated from the other metathesis products to provide a highly pure functionalized monounsaturated alkene composition which may be an acid, ester, or carboxylate salt. The monounsaturated alkene composition may be useful, for example, as a starting material in the preparation of organic chemicals.

Starting Composition (Step (a)):

As a starting composition, the method of the present invention uses compositions comprising polyunsaturated alkenes, for example, polyunsaturated fatty acids, polyunsaturated fatty esters, and carboxylate salts of polyunsaturated fatty acids. Mixtures of the foregoing may also be useful. As used herein the term "polyunsaturated fatty acid" refers to compounds that have a polyunsaturated alkene chain with a terminal carboxylic acid group. The alkene chain may be a linear or branched and may optionally include one or more functional groups in addition to the carboxylic acid group. For example, some polyunsaturated fatty acids include

one or more hydroxyl groups. The polyunsaturated alkene chain typically contains about 4 to about 30 carbon atoms, more typically about 4 to about 22 carbon atoms. In many embodiments, the alkene chain contains 18 carbon atoms (i.e., a C18 fatty acid). The unsaturated fatty acids have at least two carbon-carbon double bonds in the alkene chain. In exemplary embodiments, the polyunsaturated fatty acid has from 2 to 3 carbon-carbon double bonds in the alkene chain.

Also useful as starting compositions are polyunsaturated fatty esters. As used herein the term "polyunsaturated fatty ester" refers to compounds that have a polyunsaturated alkene chain with a terminal ester group. The alkene chain may be linear or branched and may optionally include one or more functional groups in addition to the ester group. For example, some polyunsaturated fatty esters include one or more hydroxyl groups in addition to the ester group. For example, some polyunsaturated fatty esters include one or more hydroxyl groups. Polyunsaturated fatty esters include "polyunsaturated monoesters" and "polyunsaturated polyol esters". Polyunsaturated monoesters comprise a polyunsaturated fatty acid that is esterified to a monofunctional alcohol. Polyunsaturated polyol esters have at least one polyunsaturated fatty acid that is esterified to a polyol (e.g., ethylene glycol, propylene glycol, glycerol, trimethylolpropane, erythritol, sorbitol etc). The alkene chain of polyunsaturated monoesters or polyol esters typically contains about 4 to about 30 carbon atoms, more typically about 4 to 22 carbon atoms. In exemplary embodiments, the alkene chain contains 18 carbon atoms (i.e., a C18 fatty ester). Being polyunsaturated, the alkene chain in polyunsaturated monoesters have at least two carbon-carbon double bonds and may have more than two double bonds. In exemplary embodiments, the unsaturated fatty ester has 2 to 3 carbon-carbon double bonds in the alkene chain. In polyol esters, at least one fatty acid in the polyol ester is a polyunsaturated fatty acid. The remaining fatty acids making up the polyol ester may be saturated or monounsaturated.

Also useful as a starting composition are metal salts of unsaturated fatty acids (i.e., carboxylate salts of unsaturated fatty acids). The metal salts may be salts of alkali metals (e.g., a group IA metal such as Li, Na, K, Rb, and Cs); alkaline earth metals (e.g., group IIA metals such as Be, Mg, Ca, Sr, and Ba); group IIIA metals (e.g., B, Al, Ga, In, and Tl); group IVA metals (e.g., Sn and Pb), group VA metals

(e.g., Sb and Bi), transition metals (e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Ag and Cd), lanthanides or actinides.

In many embodiments, the polyunsaturated fatty acid, ester, or carboxylate salt has a straight alkene chain and can be represented by the general formula:

$$CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$$

where:

R is hydrogen (fatty acid), an aliphatic group (fatty ester), or a metal ion (carboxylate salt);

n1 is an integer equal to or greater than 0 (typically 0 to 15; more typically 0, 3, or 6);

n2 is an integer equal to or greater than 0 (typically 2 to 11; more typically 3, 4, 7, 9, or 11);

n3 is an integer equal to or greater than 0 (typically 0 to 6; more typically 1); and

x is an integer equal to or greater than 2 (typically 2 to 6, more typically 2 to 3).

A summary of some polyunsaturated fatty acids and esters is provided in TABLE A.

TABLE A: Unsaturated Fatty Acids/Esters

| Type | General Formula | Examples of fatty acids | Examples of fatty esters |
|---|---|---|---|
| Polyunsaturated | Diunsaturated<br>$CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$<br>Where x is 2, and n1, n2, n3, and R are as described above. | Linoleic acid (x=2, n1= 3; n2 = 7; n3 = 1; and R is H.) | Methyl Linoleate (x=2, n1= 3; n2 = 7; n3 = 1; and R is CH3.) |
| | Triunsaturated<br>$CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$<br>Where x is 3, and n1, n2, n3, and R are as described above. | Linolenic acid (x=3, n1= 0; n2 = 7; n3 = 1; and R is H.) | Methyl Linolenate (x=3, n1= 0 ; n2 = 7; n3 = 1; and R is CH3.) |

Polyunsaturated monoesters may be alkyl esters (e.g., methyl esters) or aryl esters and may be derived from polyunsaturated fatty acids or polyunsaturated glycerides by transesterifying with a monohydric alcohol. The monohydric alcohol may be any monohydric alcohol that is capable of reacting with the unsaturated free fatty acid or unsaturated glyceride to form the corresponding unsaturated monoester. In some embodiments, the monohydric alcohol is a C1 to C20 monohydric alcohol, for example, a C1 to C12 monohydric alcohol, a C1 to C8 monohydric alcohol, or a C1 to C4 monohydric alcohol. The carbon atoms of the monohydric alcohol may be arranged in a straight chain or in a branched chain structure, and may be substituted with one or more substituents. Representative examples of monohydric alcohols include methanol, ethanol, propanol (e.g., isopropanol), and butanol.

Transesterification of a polyunsaturated triglyceride can be represented as follows.

1 Polyunsaturated Triglyceride + 3 Alcohol → 1 Glycerol + 1-3 Polyunsaturated Monoester

Depending upon the make-up of the polyunsaturated triglyceride, the above reaction may yield one, two, or three moles of polyunsaturated monoester. Transesterification is typically conducted in the presence of a catalyst, for example, alkali catalysts, acid catalysts, or enzymes. Representative alkali transesterification catalysts include NaOH, KOH, sodium and potassium alkoxides (e.g., sodium methoxide), sodium ethoxide, sodium propoxide, sodium butoxide. Representative acid catalysts include sulfuric acid, phosphoric acid, hydrochloric acid, and sulfonic acids. Heterogeneous catalysts may also be used for transesterification. These include alkaline earth metals or their salts such as CaO, MgO, calcium acetate, barium acetate, natural clays, zeolites, Sn, Ge or Pb, supported on various materials such as ZnO, MgO, $TiO_2$, activated carbon or graphite, and inorganic oxides such as alumina, silica-alumina, boria, oxides of P, Ti, Zr, Cr, Zn, Mg, Ca, and Fe. In exemplary embodiments, the triglyceride is transesterified with methanol ($CH_3OH$) in order to form free fatty acid methyl esters.

In some embodiments, the polyunsaturated fatty esters are polyunsaturated polyol esters. As used herein the term "polyunsaturated polyol ester" refers to compounds that have at least one polyunsaturated fatty acid that is esterified to the hydroxyl group of a polyol. The other hydroxyl groups of the polyol may be unreacted, may be esterified with a saturated fatty acid, or may be esterified with a monounsaturated fatty acid. Examples of polyols include glycerol and 1, 3 propanediol. In many embodiments, unsaturated polyol esters have the general formula:

$$R(O\text{-}Y)_m(OH)_n(O\text{-}X)_b$$

where

R is an organic group having a valency of (n+m+b);

m is an integer from 0 to (n+m+b-1), typically 0 to 2;

b is an integer from 1 to (n+m+b), typically 1 to 3;

n is an integer from 0 to (n+m+b-1), typically 0 to 2;

(n+m+b) is an integer that is 2 or greater;

X is $-(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$;

Y is $-(O)C\text{-}R'$;

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is an integer equal to or greater than 0 (typically 0 to 15; more typically 0, 3, or 6);

n2 is an integer equal to or greater than 0 (typically 2 to 11; more typically 3, 4, 7, 9, or 11);

n3 is an integer equal to or greater than 0 (typically 0 to 6; more typically 1); and

x is an integer equal to or greater than 2 (typically 2 to 6, more typically 2 to 3).

In many embodiments, the polyunsaturated polyol esters are polyunsaturated glycerides. As used herein the term "polyunsaturated glyceride" refers to a polyol ester having at least one (e.g., 1 to 3) polyunsaturated fatty acid that is esterified to a

molecule of glycerol. The fatty acid groups may be linear or branched and may include pendant hydroxyl groups. In many embodiments, polyunsaturated glycerides are represented by the general formula:

$$CH_2A\text{-}CHB\text{-}CH_2C$$

where –A; –B; and –C are selected from

–OH;

$–O(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$; and

–O(O)C-R′;

with the proviso that at least one of –A, -B, or –C is

$–O(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$.

In the above formula:

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is an integer equal to or greater than 0 (typically 0 to 15; more typically 0, 3, or 6);

n2 is an integer equal to or greater than 0 (typically 2 to 11; more typically 3, 4, 7, 9, or 11);

n3 is an integer equal to or greater than 0 (typically 0 to 6; more typically 1); and

x is an integer equal to or greater than 2 (typically 2 to 6, more typically 2 to 3).

Polyunsaturated glycerides having two –OH groups (e.g., -A and –B are –OH) are commonly known as unsaturated monoglycerides. Unsaturated glycerides having one –OH group are commonly known as unsaturated diglycerides. Unsaturated glycerides having no –OH groups are commonly known as unsaturated triglycerides.

As shown in the formula above, the polyunsaturated glyceride may include monounsaturated fatty acids, polyunsaturated fatty acids, and saturated fatty acids that are esterified to the glycerol molecule. The main chain of the individual fatty acids may have the same or different chain lengths. Accordingly, the unsaturated

glyceride may contain up to three different fatty acids so long as at least one fatty acid is a polyunsaturated fatty acid.

In many embodiments, useful starting compositions are derived from natural oils such as plant-based oils or animal fats. Representative examples of plant-based oils include canola oil, rapeseed oil, coconut oil, corn oil, cottonseed oil, olive oil, palm oil, peanut oil, safflower oil, sesame oil, soybean oil, sunflower oil, linseed oil, palm kernel oil, tung oil, castor oil, tall oil, and the like. Representative examples of animal fats include lard, tallow, chicken fat (yellow grease), and fish oil. Other useful oils include tall oil and algae oil.

In many embodiments, the plant-based oil is soybean oil. Soybean oil comprises unsaturated glycerides, for example, in many embodiments about 95% weight or greater (e.g., 99% weight or greater) triglycerides. Major fatty acids making up soybean oil include saturated fatty acids, for example, palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid), and unsaturated fatty acids, for example, oleic acid (9-octadecenoic acid), linoleic acid (9, 12-octadecadienoic acid), and linolenic acid (9,12,15-octadecatrienoic acid). Soybean oil is a highly unsaturated vegetable oil with many of the triglyceride molecules having at least two unsaturated fatty acids.

In many embodiments, the starting composition comprises about 5% weight or greater of polyunsaturated fatty acids, polyunsaturated fatty esters, or carboxylate salts of polyunsaturated fatty acids.

In many embodiments, the starting composition comprises a Δ9 polyunsaturated fatty acid, a Δ9 polyunsaturated fatty ester (e.g., monoesters or polyol esters), a carboxylate salt of a Δ9 polyunsaturated fatty acid, or mixtures of two or more of the foregoing. Δ9 polyunsaturated starting compositions have at least two carbon-carbon double bonds with one of the carbon-carbon double bonds being located between the 9$^{th}$ and 10$^{th}$ carbon atoms (i.e., between C9 and C10) in the alkene chain of the polyunsaturated fatty acid, ester, or carboxylate salt. In determining this position, the alkene chain is numbered starting with the carbon atom in the carbonyl group of the unsaturated fatty acid, ester, or salt. Included within the definition of Δ9 polyunsaturated fatty acids, esters, and carboxylate salts

are Δ9, 12 polyunsaturated fatty acids, esters and carboxylate salts, and Δ9, 12, 15 polyunsaturated fatty acids, esters and carboxylate salts.

In many embodiments, the Δ9 unsaturated starting materials have a straight alkene chain and may be represented by the general structure:

$$CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_7\text{-}COOR$$

where

R is hydrogen (fatty acid), an aliphatic group (fatty monoester) or a metal ion (carboxylate salt);

n1 is an integer equal to or greater than 0 (typically 0 to 6; more typically 0, 3, 6);

n3 is an integer equal to or greater than 0 (typically 1); and

x is an integer equal to or greater than 2 (typically 2 to 6, more typically 2 to 3).

In exemplary embodiments, the Δ9 polyunsaturated starting materials have a total of 18 carbons in the alkene chain. Examples include

$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOR; \text{ and}$$
$$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOR.$$

where R is hydrogen (fatty acid), an aliphatic group (fatty monoester) or a metal ion (fatty acid salt);

Δ9 unsaturated fatty esters may be monoesters or polyol esters. In many embodiments, the Δ9 unsaturated polyol esters have the general structure

$$CH_2A\text{-}CHB\text{-}CH_2C$$

where –A; –B; and –C are independently selected from

–OH;

-O(O)C-R′; and

$-O(O)C\text{-}(CH_2)_7\text{-}[\text{-}CH{=}CH\text{-}CH_2\text{-}]_x\text{-}(CH_2)_{n1}CH_3$

with the proviso that at least one of –A, -B, or –C is

$-O(O)C-(CH_2)_7-[-CH=CH-CH_2-]_{x}-(CH_2)_{n1}CH_3$

In the above formula:

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is independently an integer equal to or greater than 0 (typically 0 to 6); and

x is an integer greater than or equal to 2 (typically 2 to 6, more typically 2 to 3).

In exemplary embodiments, the starting composition comprises one or more C18 fatty acids, for example, linoleic acid (i.e., 9, 12-octadecadienoic acid) and linolenic acid (i.e., 9, 12, 15-octadecatrienoic acid). In other exemplary embodiments, the starting composition comprises one or more C18 fatty esters, for example, methyl linoleate and methyl linolenate. In yet another exemplary embodiment, the starting composition comprises an unsaturated glyceride comprising Δ9 fatty acids, for example, C18 Δ9 fatty acids.

Δ9 starting compositions may be derived, for example, from vegetable oils such as soybean oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, sunflower oil, canola oil, safflower oil, palm oil, palm kernel oil, linseed oil, castor oil, olive oil, peanut oil, and the like. Since these vegetable oils yield predominately the glyceride form of the Δ9 unsaturated fatty esters, the oils must be processed (e.g., by transesterification) to yield an unsaturated free fatty ester, an unsaturated fatty acid, or salt. Δ9 unsaturated fatty acids, esters, and salts may also be also be derived from tall oil, fish oil, lard, and tallow. A summary of some useful starting compositions is provided in TABLE B.

TABLE B

| Starting Composition | Description | Classification | Bond Locations |
|---|---|---|---|
| Linoleic acid | C18 diunsaturated fatty acid (C18:2) | Δ9 | Δ9, 12 |
| Linolenic acid | C18 triunsaturated fatty acid (C18:3) | Δ9 | Δ9, 12, 15 |
| Alkyl linoleate | C18 diunsaturated fatty ester (C18:2) | Δ9 | Δ9, 12 |
| Alkyl linolenate | C18 triunsaturated fatty ester (C18:3) | Δ9 | Δ9, 12, 15 |
| Vegetable Oil (e.g., soybean oil) | Unsaturated glycerides of C18:1, C18:2, and C18:3 fatty acids | Δ9 | Δ9<br>Δ9, 12<br>Δ9, 12, 15 |

Cross-Metathesis (Step (b)):

According to the method of the invention, the starting composition is cross-metathesized with a short-chain olefin in the presence of a metathesis catalyst to form cross-metathesis products comprising: (i) one or more olefin compounds; and (ii) one or more acid-, ester-, or carboxylate salt-functionalized monounsaturated alkenes. In many embodiments, a molar excess of the short-chain internal olefin is reacted with the starting composition.

Short-chain olefins are short chain length organic compounds that have at least one carbon-carbon double bond. In many embodiments, the short chain olefins have between about 3 and about 9 carbon atoms. Short chain olefins can be represented by the structure (II):

$$R^7R^8C{=}CR^9R^{10}$$

(II)

where $R^7$, $R^8$, $R^9$, and $R^{10}$ are each, independently, hydrogen or an organic group, with the proviso that at least one of $R^7$ or $R^8$ is an organic group.

The organic group may be an aliphatic group, an alicyclic group, or an aromatic group. Organic groups may optionally include heteroatoms (e.g., O, N, or S atoms), as well as functional groups (e.g., carbonyl groups). The term aliphatic group means a saturated or unsaturated, linear or branched, hydrocarbon group. This term is used to encompass alkyl groups. The term alkyl group means a monovalent, saturated, linear, branched, or cyclic hydrocarbon group. Representative examples include of alkyl groups include methyl, ethyl, propyl (n-propyl or i-propyl), butyl (n-butyl or t-butyl), pentyl, hexyl, and heptyl. An alicyclic group is an aliphatic group arranged in one or more closed ring structures. The term is used to encompass saturated (i.e., cycloparaffins) or unsaturated (cycloolefins or cycloacetylenes) groups. An aromatic or aryl group is an unsaturated cyclic hydrocarbon having a conjugated ring structure. Included within aromatic or aryl groups are those possessing both an aromatic ring structure and an aliphatic or alicyclic group.

In many embodiments, the short-chain olefin is a short-chain internal olefin. Short-chain internal olefins may be represented by structure (II):

$$R^7R^8C{=}CR^9R^{10}$$

(II)

where $R^7$, $R^8$, $R^9$, and $R^{10}$ are each, independently, hydrogen or an organic group, with the proviso that at least one of $R^7$ or $R^8$ is an organic group, and at least one of $R^9$ or $R^{10}$ is an organic group.

Short-chain internal olefins may be symmetric or asymmetric. Symmetric short-chain internal olefins having one carbon-carbon double bond may be represented by structure (II-A):

$$R^7CH{=}CHR^9$$

(II-A)

where $-R^7$ and $-R^9$ are same organic group.

Representative examples of symmetric short-chain internal olefins include 2-butene, 3-hexene, and 4-octene. In some embodiments, the short-chain internal olefin is asymmetric. Representative examples of asymmetric short-chain internal olefins include 2-pentene, 2-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 2-nonene, 3-nonene, and 4-nonene.

In many embodiments, symmetric short-chain internal olefins are preferred for cross-metathesis because the cross-metathesis products that result will include fewer products than if an asymmetric short-chain internal olefin is used for cross-metathesis. For example, as shown below, when a first double-bond containing compound (i.e., A=B) is cross-metathesized with a symmetric short-chain internal olefin (i.e., represented by C=C), two cross-metathesis products are produced. By contrast, when the same double-bond containing compound is cross-metathesized with an asymmetric short-chain internal olefin (i.e., represented by C=D), four cross-metathesis products are produced.

Metathesis of Symmetric Short-chain Internal Olefin (C=C)

$$A{=}B + C{=}C \leftrightarrow A{=}C + B{=}C$$

Metathesis of Asymmetric Short-chain Internal Olefin (C=D):

$$A{=}B + C{=}D \leftrightarrow A{=}C + B{=}C + A{=}D + B{=}D$$

In some embodiments, the short-chain olefin is an α-olefin. Alpha olefins are included in general structure (II) when $R^7$, $R^8$, and $R^9$ are all hydrogen. Representative α-olefin are shown in general structure (II-B):

$$CH_2{=}CH\text{-}R^{10}$$

(II-B)

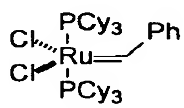
where $-R^{10}$ is an organic group.

Representative $-R^{10}$ groups include $-(CH_2)_n-CH_3$, where n ranges from 0 to 6. Exemplary alpha olefin compounds include 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-nonene.

Metathesis Catalysts:

The metathesis reaction is conducted in the presence of a catalytically effective amount of a metathesis catalyst. The term "metathesis catalyst" includes any catalyst or catalyst system which catalyzes the metathesis reaction.

Any known or future-developed metathesis catalyst may be used, alone or in combination with one or more additional catalysts. Exemplary metathesis catalysts include metal carbene catalysts based upon transition metals, for example, ruthenium, molybdenum, osmium, chromium, rhenium, and tungsten.. Exemplary ruthenium-based metathesis catalysts include those represented by structures 12 (commonly known as Grubbs's catalyst), 14 and 16, where Ph is phenyl, Mes is mesityl, and Cy is cyclohexyl.



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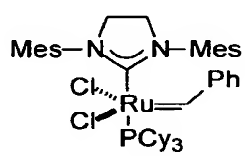

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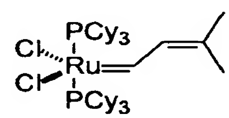

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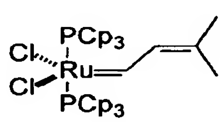
Structures 18, 20, 22, 24, 26, and 28, illustrated below, represent additional ruthenium-based metathesis catalysts, where Ph is phenyl, Mes is mesityl, py is pyridine, Cp is cyclopentyl, and Cy is cyclohexyl. Techniques for using catalysts 12, 14, 16, 18, 20, 22, 24, 26, and 28, as well as additional related metathesis catalysts, are known in the art.



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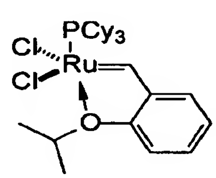

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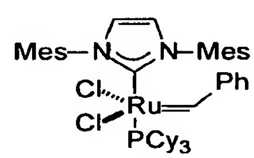

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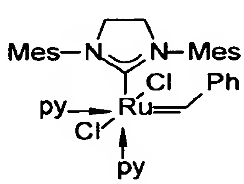

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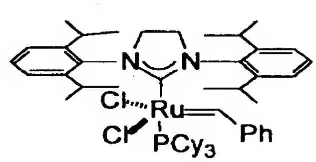

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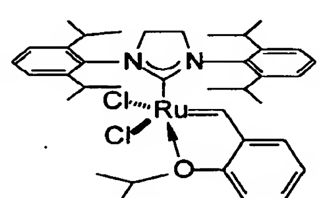

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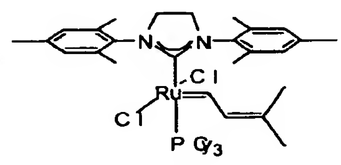
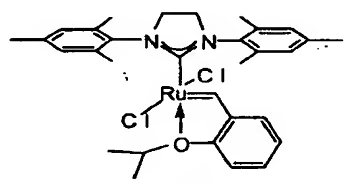
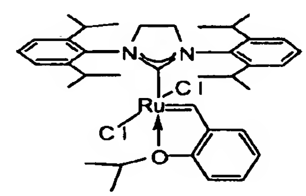
Catalysts C627, C682, C697, C712, and C827 are additional ruthenium-based catalysts, where Cy is cyclohexyl in C827.



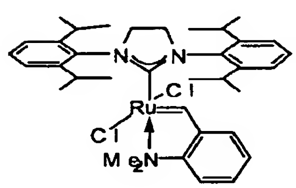
C827



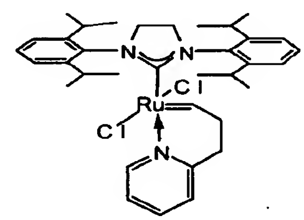
C627



C712



C697



C682

Additional exemplary metathesis catalysts include, without limitation, metal carbene complexes selected from the group consisting of molybdenum, osmium, chromium, rhenium, and tungsten. The term "complex" refers to a metal atom, such as a transition metal atom, with at least one ligand or complexing agent coordinated or bound thereto. Such a ligand typically is a Lewis base in metal carbene complexes useful for alkyne or alkene-metathesis. Typical examples of such ligands include phosphines, halides and stabilized carbenes. Some metathesis catalysts may employ plural metals or metal co-catalysts (e.g., a catalyst comprising a tungsten halide, a tetraalkyl tin compound, and an organoaluminum compound).

An immobilized catalyst can be used for the metathesis process. An immobilized catalyst is a system comprising a catalyst and a support, the catalyst associated with the support. Exemplary associations between the catalyst and the support may occur by way of chemical bonds or weak interactions (e.g. hydrogen bonds, donor acceptor interactions) between the catalyst, or any portions thereof, and the support or any portions thereof. Support is intended to include any material suitable to support the catalyst. Typically, immobilized catalysts are solid phase catalysts that act on liquid or gas phase reactants and products. Exemplary supports are polymers, silica or alumina. Such an immobilized catalyst may be used in a flow process. An immobilized catalyst can simplify purification of products and recovery of the catalyst so that recycling the catalyst may be more convenient.

The metathesis process can be conducted under any conditions adequate to produce the desired metathesis products. For example, stoichiometry, atmosphere, solvent, temperature and pressure can be selected to produce a desired product and to minimize undesirable byproducts. The metathesis process may be conducted under an inert atmosphere. Similarly, if the olefin reagent is supplied as a gas, an inert gaseous diluent can be used. The inert atmosphere or inert gaseous diluent typically is an inert gas, meaning that the gas does not interact with the metathesis catalyst to substantially impede catalysis. For example, particular inert gases are selected from the group consisting of helium, neon, argon, nitrogen and combinations thereof.

Similarly, if a solvent is used, the solvent chosen may be selected to be substantially inert with respect to the metathesis catalyst. For example, substantially inert solvents include, without limitation, aromatic hydrocarbons, such as benzene, toluene, xylenes, etc.; halogenated aromatic hydrocarbons, such as chlorobenzene and dichlorobenzene; aliphatic solvents, including pentane, hexane, heptane, cyclohexane, etc.; and chlorinated alkanes, such as dichloromethane, chloroform, dichloroethane, etc.

In certain embodiments, a ligand may be added to the metathesis reaction mixture. In many embodiments using a ligand, the ligand is selected to be a molecule that stabilizes the catalyst, and may thus provide an increased turnover number for the catalyst. In some cases the ligand can alter reaction selectivity and

product distribution. Examples of ligands that can be used include Lewis base ligands, such as, without limitation, trialkylphosphines, for example tricyclohexylphosphine and tributyl phosphine; triarylphosphines, such as triphenylphosphine; diarylalkylphosphines, such as, diphenylcyclohexylphosphine; pyridines, such as 2,6-dimethylpyridine, 2,4,6-trimethylpyridine; as well as other Lewis basic ligands, such as phosphine oxides and phosphinites. Additives may also be present during metathesis that increase catalyst lifetime.

Any useful amount of the selected metathesis catalyst can be used in the process. For example, the molar ratio of the unsaturated polyol ester to catalyst may range from about 5:1 to about 10,000,000:1 or from about 50:1 to 500,000:1.

The metathesis reaction temperature may be a rate-controlling variable where the temperature is selected to provide a desired product at an acceptable rate. The metathesis temperature may be greater than -40°C, may be greater than about -20°C, and is typically greater than about 0°C or greater than about 20°C. Typically, the metathesis reaction temperature is less than about 150°C, typically less than about 120°C. An exemplary temperature range for the metathesis reaction ranges from about 20°C to about 120°C.

The metathesis reaction can be run under any desired pressure. Typically, it will be desirable to maintain a total pressure that is high enough to keep the cross-metathesis reagent in solution. Therefore, as the molecular weight of the cross-metathesis reagent increases, the lower pressure range typically decreases since the boiling point of the cross-metathesis reagent increases. The total pressure may be selected to be greater than about 10kPa, in some embodiments greater than about 30 kP, or greater than about 100kPa. Typically, the reaction pressure is no more than about 7000 kPa, in some embodiments no more than about 3000 kPa. An exemplary pressure range for the metathesis reaction is from about 100 kPa to about 3000 kPa.

In some embodiments, the metathesis reaction is catalyzed by a system containing both a transition and a non-transition metal component. The most active and largest number of catalyst systems are derived from Group VI A transition metals, for example, tungsten and molybdenum.

Separation Step (step (c)):

After cross-metathesis with a short-chain olefin at least a portion of one of the resulting monounsaturated alkenes are separated from the remaining cross-metathesis products. In embodiments where the short chain olefin is asymmetric more than one monofunctional alkene is formed during the cross-metathesis reaction. For example, the cross metathesis of $CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$ with short chain olefin $R^7R^8C{=}CR^9R^{10}$ results in two monofunctional alkenes having the general structure:

$$R^7R^8C{=}CH\text{-}(CH_2)_{n2}\text{-}COOR$$

and

$$R^9R^{10}C{=}CH\text{-}(CH_2)_{n2}\text{-}COOR$$

where R is hydrogen (fatty acid), an aliphatic group (fatty monoester) or a metal ion (carboxylate salt);
n2 is an integer equal to or greater than 0 (typically 2 to 11; more typically 3, 4, 7, 9, or 11); and
$R^7$, $R^8$, $R^9$, and $R^{10}$ are each, independently, hydrogen or an organic group.

In embodiments where the short chain internal olefin is symmetric, the cross-metathesis reaction results in the formation of a single monounsaturated alkene compound. For example, the cross metathesis of $CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$ with short chain olefin $R^7R^8C{=}CR^7R^8$ results a monofunctional alkene having the general structure:

$$R^7R^8C{=}CH\text{-}(CH_2)_{n2}\text{-}COOR$$

where R is hydrogen (fatty acid), an aliphatic group (fatty monoester) or a metal ion (carboxylate salt);
n2 is an integer equal to or greater than 0 (typically 2 to 11; more typically 3, 4, 7, 9, or 11); and
$R^7$ and $R^8$ are each hydrogen or an organic group.

In one exemplary embodiment, the starting material is a Δ9 starting composition and the short-chain internal olefin is 2-butene. In this embodiment, the monounsaturated alkene composition comprises $CH_3$-CH=CH-$(CH_2)_7$-COOR; where R is hydrogen (fatty acid), an aliphatic group (fatty ester), or a metal ion (carboxylate salt).

In another exemplary embodiment, the starting material is a Δ9 starting composition and the short-chain internal olefin is 3-hexene. In this embodiment, the monounsaturated alkene composition comprises: $CH_3$-$CH_2$-CH=CH-$(CH_2)_7$-COOR; where R is hydrogen (fatty acid), an aliphatic group (fatty ester), or a metal ion (carboxylate salt).

In yet another exemplary embodiment, the starting material is a Δ9 starting composition and the short-chain internal olefin is 1-propene. In this embodiment, the monounsaturated alkene composition comprises a mixture of: $CH_2$=CH-$(CH_2)_7$-COOR and $CH_3$-CH=CH-$(CH_2)_7$-COOR; where R is independently hydrogen (fatty acid), an aliphatic group (fatty ester), or a metal ion (carboxylate salt).

In yet another exemplary embodiment, the short-chain internal olefin is 1-butene and the monounsaturated alkene composition comprises a mixture of: $CH_2$=CH-$(CH_2)_7$-COOR and $CH_3$-$CH_2$-CH=CH-$(CH_2)_7$-COOR; where R is independently hydrogen (fatty acid), an aliphatic group (fatty ester), or a metal ion (carboxylate salt).

Useful techniques for separating the monounsaturated alkene include, for example, distillation, reactive distillation, chromatography, fractional crystallization, membrane separation, liquid/liquid extraction, or a combination thereof.

In many embodiments, the separated monounsaturated alkene has a purity level of about 95% weight or greater, for example, about 96% weight or greater, about 97% weight or greater, about 98% weight or greater, about 99% weight or greater, or about 99.5% weight or greater.

The method of the invention will now be described with reference to a specific illustrative embodiment. In this embodiment, a representative starting composition comprising a mixture of methyl oleate, methyl linoleate, and methyl linolenate is cross-metathesized with 2-butene to provide cross-metathesis products

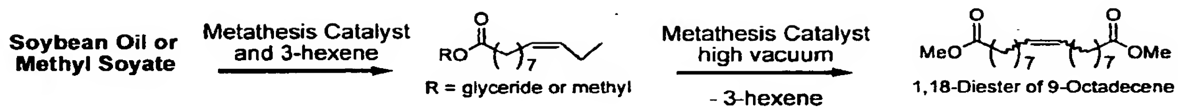
including the monounsaturated alkene compound 9-undecenoic acid methyl ester ($CH_3$-CH=CH-$(CH_2)_7$-$COOCH_3$).

Referring now to FIG. 3, the starting composition comprises methyl oleate, methyl linoleate, and methyl linolenate. As shown in FIG. 3, methyl oleate, methyl linoleate, and methyl linolenate each include one or more carbon-carbon double bonds. According to the method, the starting composition is cross metathesized with a short-chain olefin 20 (here 2-butene) in the presence of a metathesis catalyst (not shown). Metathesis of the starting composition takes place at the carbon-carbon double bonds that are present in the starting composition. For example, as shown in FIG 1, methyl oleate reacts with 2-butene to form the methyl ester of 9-undecenoic acid and the olefin compound 2-undecene. In similar fashion, the starting material methyl linoleate reacts with 2 moles of 2-butene to form the methyl ester of 9-undecenoic acid and the olefin compound 2, 5-heptadiene and 2-octene. Since methyl linoleate has two carbon-carbon double bonds, metathesis results in more than one olefin compound being formed, with each corresponding to cross-metathesis at one of the carbon-carbon double bonds. As shown in FIG. 3, the starting material methyl linolenate reacts with 3 moles of 2-butene to form the methyl ester of 9-undecenoic acid along with 2 moles of 2, 5-heptadiene and 1 mole of 2-pentene. After completion of the cross-metathesis, the monounsaturated compound 9-undecenoic acid methyl ester can be separated at high purity from the remaining cross-metathesis products using conventional separation techniques such as distillation. The resulting 9-undecenoic acid methyl ester may be used as the starting material in the production of industrially important organic compounds such as diacids.

The invention will now be described with reference to the following non-limiting examples.

## EXAMPLES

EXAMPLE 1:Synthesis of 1, 18-Diester (1,18-dimethyl ester of 9-octadecene) from 3-Hexene and Soybean Oil




Production of Methyl 9-dodecenoate [$CH_3CH_2CH{=}CH(CH_2)_7COO_2CH_3$]

Metathesis reactions were conducted in a 250 ml 3-neck round bottom Schlenk flask that was equipped with a reflux condenser (connected to a bubbler), two septa, a stir bar, and a thermocouple. Prior to adding any reactants, the apparatus was degassed with argon for thirty minutes. Then, 70 ml (64.4 g) of degassed soybean oil (Cargill soybean oil (Salad oil), Lot # F4102) was added to the apparatus. In a separate container, 3-hexene was degassed with argon for one hour. Following degassing, 127 ml (86.4 grams) of the degassed 3-hexene was added to the flask using a graduated cylinder. The resulting mixture was degassed for fifteen minutes with argon. The mixture was then heated to 65°C before adding the metathesis catalyst.

Metathesis catalyst (C827, Lot # 067-050B) was added to the degassed mixture of soybean oil and 3-hexene in the amount shown in TABLE 1. In each case, the resulting mixture was allowed to react at 65°C, with aliquots taken at 2, 4, and 6 hours to check for conversion using a gas chromatograph. Maximum conversion was reached after two hours in all cases. In each case, after reacting for 6 hours, 1.30 grams of activated clay (Pure-Flo B80 natural Bleaching Adsorbent) was added, and the resulting composition was stirred overnight. Following this, the composition was filtered through a bed of silica to remove the activated clay and metathesis catalyst. The filtrates were sealed in a sample bottle and refrigerated. Percent yield of methyl 9-dodecenoate was determined using a gas chromatograph. The resulting data is presented in TABLE 1.

TABLE 1

| Example No. | Catalyst Loading[1] (ppm) | % Yield of Methyl 9-dodecenoate[2] |
|---|---|---|
| 1-1 | 100 | 33.7 |
| 1-2 | 75 | 40.1 |
| 1-3 | 50 | 30.5 |
| 1-4 | 100 | 33.0 |

[1]Catalyst 827 loading in ppm per double bond of SBO. 3-Hexene was added in 3 equivalents per double bond of SBO.

[2]GC yield after 2 hours, yields did not change significantly at 6 hours.

EXAMPLE 2: Vacuum Distillation of $9C_{12}O_2Me$.

A glass 2.0 L 3-necked round bottom flask with a magnetic stirrer, packed column, distillation head, and temperature controller was charged with esterified products and was placed in a heating mantle. The flask was attached to a 2-inch x 36-inch glass distillation packed column containing 0.16" Pro-Pak™ stainless steel saddles. The distillation column was connected to a fractional distillation head, which was connected to a vacuum line. A 500 mL pre-weighed round bottom flask was used to collect the distilled fractions. During distillation, vacuum was applied to provide a pressure of <1 mmHg. TABLE 2 contains the vacuum distillation results.

TABLE 2: Distillation Data

| Distillation Fraction | Distillation Head Temperature (°C) | Pot Temperature (°C) | Isolated Weight (grams) | GC Retention Time (min) |
|---|---|---|---|---|
| $3C_9 + 3,6\ C_9$ | 26 | 37 | 136.5 | 1.6 |
| $3C_{12} + 3,6\ C_{12}$ | 48 | 58 | 125.4 | 3.87 |
| $6C_{15} + 6,9\ C_{15}$ | 92-94 | 115-120 | 68 | 7.45 |
| $9C_{12}$-$O_2Me$ | 93-96 | 120-122 | 275.4 | 7.88 |

$6C_{15}$ + $6,9C_{15}$ impurities were separated from $9C_{12}O_2Me$ by equilibrating the distillation column for 24 hours, followed by collecting $6C_{15}$ + $6,9C_{15}$ with a reflux ratio of 1:10 (i.e. 1 drop collected for every 10 drops sent back to the packed column). This procedure demonstrates that $9C_{12}O_2Me$ (275.4 g.) could be isolated in 50.9% yield and in 99.2% chemical purity. The $6C_{15}$ + $6,9C_{15}$ impurities could be removed by fractional distillation.

The following general procedures are applicable for EXAMPLES 3-9.

<u>General procedure for the cross-metatheses of olefinic substrate and alpha-olefin</u>:

Terminal olefins were synthesized by the cross metathesis of short chained alpha-olefins and seed oils with a ruthenium metathesis catalyst. The short chained alpha-olefins include olefin preferred having 8 or less carbon atoms, such as as 1-propene, 1-butene, 1-pentene, etc. but >9 carbon alpha olefins are acceptable. Seed oils include triacylglycerides, as in soybean oil, fatty acid esters, as in jojoba oil and FAMES, such as methyl esters of soybean oil (soy FAME).

When the alpha-olefin used was a gas under ambient conditions (e.g., 1-propene and 1-butene), a procedure analogous to that used for the ethenolysis was also employed. As such, a Fisher-Porter bottle equipped with a stir bar was charged with the olefinic substrate. A solution of olefin metathesis catalyst of an appropriate concentration was prepared in anhydrous dichloromethane (from Aldrich) and the desired volume of this solution added to the olefinic substrate. The head of the Fisher-Porter bottle was equipped with a pressure gauge and a dip-tube was adapted on the bottle. The system was sealed and taken out of the glove box to a gas line. The vessel was then purged 3 times with the gas (e.g., 1-propene and 1-butene), pressurized to the indicated pressure (about 50 to about 150 psi for 1-propene and about 30 to about 90 psi for 1-butene) and placed in an oil bath at the indicated temperature. The reaction was monitored by following the method described above. When the alpha-olefin used was a liquid under ambient conditions (e.g., 1-octene), the olefinic substrate and the alpha-olefin were mixed in an oven-dried 20 mL vial equipped with a stir bar. The vial was sealed with a Teflon-seal cap and the olefinic substrate/alpha-olefin mixture was brought to the indicated temperature, so that the reactions are conducted under a slightly positive pressure (from 1.1 to about 2 atm, i.e. from 16 psi to about 30 psi). A solution of olefin metathesis catalyst of an

appropriate concentration was prepared in anhydrous dichloromethane (from Aldrich) and the desired volume of this solution added to the olefinic substrate/alpha-olefin mixture via syringe through the Teflon-seal while stirring. The reaction mixture was kept at the desired temperature for the indicated period of time before adding a 1.0 M solution of THMP (1 mL) via syringe through the Teflon-seal cap. The mixture was then heated at 60 °C for 1 hour, diluted with 5 mL of distilled water and 5 mL of hexanes and the organic phase was separated and analyzed by GC. If the olefinic substrate is a glyceride, it is transesterified prior to GC analysis using a method similar to the transesterification of metathesized SBO described below.

Example Procedure for the Transesterification of Metathesized SBO: A glass 3-necked round bottom flask containing a magnetic stirrer and fitted with a condenser, temperature probe, and gas adapter was charged with crude metathesized SBO product (~ 2 L) and 1% w/w NaOMe in MeOH. The resulting light yellow heterogeneous mixture was stirred at 60 °C for 1 hr. Towards the end of the hour, the mixture turned a homogeneous orange color. Esterified products were transferred into a separatory funnel and extracted with 2.0 L DI-$H_2O$. The aqueous layer was then extracted with 2 × 2.0 L $Et_2O$. The combined organic extracts were dried over anhydrous $Na_2SO_4$ (300 g) for 20 hours. The solution of esterified products was filtered and the filtrate was stripped of solvent *via* rotary evaporator.

Vacuum Distillation: A glass 2.0 L 3-necked round bottom flask with a magnetic stirrer, packed column, distillation head, and temperature controller was charged with methyl ester products and placed in a heating mantle. The flask was attached to a 2-inch x 36-inch glass distillation packed column contain 0.16" Pro-Pak™ stainless steel saddles. The distillation column was adapted to a fractional distilling head, which was connected to a vacuum line. A 500 mL pre-weighed round bottom flask was used for collecting the fractions. Vacuum on this system was <1 mmHg.

GC Analysis Conditions: The products were analyzed using an Agilent 6890 gas chromatography (GC) instrument with a flame ionization detector (FID). The following conditions and equipment were used:

Column: Rtx-5, 30m x 0.25mm (ID) x 0.25μm film thickness.

Manufacturer: Restek

| | |
|---|---|
| GC and column conditions: | Injector temperature: 250°C |
| | Detector temperature: 280°C |
| Oven temperature: | Starting temperature: 100°C, hold time: 1 min. Ramp rate 10°C/min to 250°C, hold time: 12 min. |
| Carrier gas: | Helium |
| Mean gas velocity: | 31.3 ± 3.5% cm/sec (calculated) |
| Split ratio: | ~50:1 |

The products were characterized by comparing peaks with known standards, in conjunction with supporting data from mass spectrum analysis (GCMS-Agilent 5973N). GCMS analysis was accomplished with a second Rtx-5, 30m x 0.25mm (ID) x 0.25μm film thickness GC column, using the same method as above.

TABLE 3 provides GC retention times used for identifying compounds in the examples provided below. TABLE 3 also provides compound abbreviations that are used throughout the examples.

TABLE 3. GC Analysis of Products from the Cross Metathesis of Seed Oils with 1-Propene and 1-Butene.

| Retention Time (min) | Compound | Compound Abbreviation |
|---|---|---|
| 1.300 | E-2-Octene | $2C_8$ |
| 1.596 | 3-Nonene | $3C_9$ |
| 2.039 | 1-Decene | $1C_{10}$ |
| 2.907 | E-2-Undecene | E-$2C_{11}$ |
| 3.001 | Z-2-Undecene | Z-$2C_{11}$ |
| 3.836 | 3-Dodecenes | $3C_{12}$ |
| 5.298 | Methyl 9-Decenoate | $9C_{10}O_2Me$ (9DA) |
| 6.708 | Methyl E-9-Undecenoate | E-$9C_{11}O_2Me$ (9UDA) |
| 6.852 | Methyl Z-9-Undecenoate | Z-$9C_{11}O_2Me$ (9UDA) |
| 7.419 | Pentadecadienes | $nC_{15}$ |
| 7.816 | Methyl E-9-Dodecenoate | E-$9C_{12}O_2Me$ |
| 7.894 | Methyl Z-9-Dodecenoate | Z-$9C_{12}O_2Me$ |
| 10.939 | 9-Octadecene | $9C_{18}$ |
| 11.290 | Methyl 9-12 tetradecadienoate | $9,12C_{14}O_2Me$ |
| 12.523 | Methyl palmitate | $C_{16}O_2Me$ |
| 14.306 | Methyl linoleates | $9,12C_{18}O_2Me$ |
| 14.363 | Methyl oleates | $9C_{18}O_2Me$ |
| 14.537 | Methyl stearate | $C_{18}O_2Me$ |
| 17.138 | Methyl 9, 21- Henicosadienaote | $9,12C_{18}O_2Me$ |

| Retention Time (min) | Compound | Compound Abbreviation |
|---|---|---|
| 17.586 | 1,18 Dimethyl ester of 9-Octadecene | $9,12C_{18}O_2Me$ |
| 22.236 | Methyl 9,12,15-docosatrienoate | $9,12,15C_{21}O_2Me$ |

The structure of certain metathesis catalysts referenced herein may be found, for example, in U.S. Provisional Patent Application No. 60/851,693, filed October 13, 2006, and entitled "Synthesis of Terminal Alkenes from Internal Alkenes Via Olefin Metathesis" (Schrodi et al.).

EXAMPLE 3

1-Propene Cross-Metathesis Reaction

Soy FAME, (Chemol, IF-24298) was flashed distilled under vacuum (< 1mm Hg). Degassed Soy FAME 7.5L (6.8 Kg, 22.9 mol) and 0.74 g (25 ppm/double bond) metathesis catalyst 827 were added to a 20L Parr Reactor under an argon atmosphere. The mixture was degassed with argon for 30 minutes. 1-Propene was added while heating to 60°C, the pressure of the reaction was between 130 psi to 150 psi. The 1-propene was added using a one-way check valve to prevent back flow into the 1-propene cylinder. After 4 hours, GC analysis indicated 9.8% 1-decene, 5.4% 2-undecene, 17.5% methyl 9-decenoate and 13.9% methyl 2-undecenoate.

The pressure was released and vented into a fume hood. When the reactor was at ambient pressure, 50 ml of 1 M THMP solution in IPA (50 mol equivalents) was added, the reactor degassed with argon and heated to 60°C overnight (~18 hr).

The reactor was cooled to room temp, ~2.5L of the reaction mixture was added to 4 L separatory funnel and washed with 1 L of water and 1 L of brine. This was repeated until the Parr reactor was emptied. The combined washed metathesis product was dried over sodium sulfate, filtered and distilled under reduced pressure.

Metathesis products were purified by vacuum distillation using a 2" x 36" distillation column packed with 0.16" stainless Pro-Pak™ distillation packing containing a vacuum distillation head. The vacuum was maintained at 2 mmHg.

TABLE 4 lists the 4 main products from the vacuum distillation of propenolysis of Soy FAME.

TABLE 4. Products from the Cross Metathesis of 1-Propene and Soy FAME[1]

| Compound | GC Area percent | Isolated Yields (g) |
|---|---|---|
| 1-Decene | 9.8% | 231.0 |
| 2-Undecene | 5.4% | 183.1 |
| Methyl 9-Decenoate | 17.5% | 547.1 [2] |
| Methyl 9-Undecenoate | 13.9% | 398.8 [3] |

[1] Metathesis Reaction #129-075 and 129-076 and Distillation Results #129-085
[2] Isolated 280.6 g of 98.0 % purity and 293.5 g of 79.7% purity
[3] Isolated 170.9g of 94.2% purity and 227.9g of 80.5% purity

EXAMPLE 4

Propenolysis of SBO

RBD soybean oil from Cargill was subjected to cross-metathesis with 1-propene using C827 according to the procedure described above. The reactions were performed at 60 °C and under 130 psi of 1-propene. The results are provided in TABLE 5.

TABLE 5. Propenolysis of SBO[1]

| Entry | Catalyst Amt. (ppm) | Time (h) | $1C_{10}$ (%) | $E\text{-}2C_{11}$ + $Z\text{-}2C_{11}$ (%) | 9DA (%) | 9UDA (%) | Yield (%) | $TON_{9DA}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 75 | 2 | 7.14 | 6.13 | 12.72 | 9.49 | 35.74 | 1696 |
| 2 | 75 | 4 | 6.63 | 4.74 | 16.76 | 10.95 | 39.08 | 2234 |
| 3 | 50 | 2 | 7.52 | 5.55 | 15.97 | 10.80 | 39.84 | 3194 |
| 4 | 50 | 4 | 8.99 | 5.38 | 21.61 | 12.30 | 48.29 | 4322 |
| 5 | 25 | 1 | 7.65 | 6.01 | 18.51 | 14.50 | 46.64 | 7403 |
| 6 | 25 | 2 | 7.31 | 6.33 | 18.70 | 16.05 | 48.39 | 7482 |
| 7 | 25 | 3 | 8.71 | 6.58 | 20.69 | 15.56 | 51.54 | 8275 |
| 8 | 25 | 4 | 8.91 | 6.60 | 21.52 | 15.82 | 52.86 | 8609 |
| 9 | 10 | 1 | 2.91 | 2.92 | 4.71 | 4.73 | 15.27 | 4705 |
| 10 | 10 | 2 | 5.68 | 4.77 | 9.50 | 8.35 | 28.30 | 9501 |
| 11 | 10 | 3 | 7.82 | 5.84 | 14.21 | 10.63 | 38.51 | 14214 |
| 12 | 10 | 4 | 7.89 | 5.40 | 15.59 | 10.89 | 39.77 | 15593 |
| 13 | 10 | 6 | 9.53 | 6.42 | 16.42 | 10.74 | 43.11 | 16423 |

[1] Percentages correspond to GC area

EXAMPLE 5

Propenolysis of Methyl Soyate

Soy FAME was subjected to cross-metathesis with 1-propene using C827 according to the procedure described above. Soy FAME obtained from Chemol was distilled and degassed by sparging with argon for 1 hour/L prior to being stored over activated alumina in a glove box under an argon atmosphere. The reactions were performed at 60 °C and under 130 psi of 1-propene (unless specified otherwise). The results are provided in TABLE 6.

TABLE 6. Propenolysis of Methyl Soyate[1]

| Entry | Catalyst Amt. (ppm) | Time (h) | $1C_{10}$ (%) | $E$-$2C_{11}$ + $Z$-$2C_{11}$ (%) | 9DA (%) | 9UDA (%) | Yield (%) | $TON_{9DA}$ |
|---|---|---|---|---|---|---|---|---|
| 1[2] | 75 | 4 | 5.60 | 4.79 | 9.69 | 8.15 | 28.23 | 1292 |
| 2 | 75 | 4 | 6.82 | 5.56 | 11.89 | 8.84 | 33.11 | 1585 |
| 3 | 25 | 1 | 10.51 | 7.73 | 22.39 | 15.68 | 56.30 | 8955 |
| 4 | 25 | 2 | 10.78 | 7.51 | 22.51 | 15.10 | 55.90 | 9006 |
| 5 | 25 | 3 | 11.06 | 7.35 | 23.72 | 14.89 | 57.01 | 9486 |
| 6 | 25 | 4 | 11.47 | 7.40 | 23.68 | 14.88 | 57.42 | 9470 |
| 7 | 10 | 0.5 | 8.67 | 6.42 | 16.36 | 11.54 | 42.99 | 16359 |
| 8 | 10 | 1 | 9.78 | 6.40 | 18.90 | 12.13 | 47.21 | 18898 |
| 9 | 10 | 2 | 10.08 | 6.43 | 19.87 | 12.33 | 48.71 | 19871 |
| 10 | 10 | 3 | 10.20 | 6.41 | 20.00 | 12.32 | 48.92 | 20001 |
| 11 | 10 | 4 | 10.17 | 6.43 | 20.13 | 12.36 | 49.10 | 20134 |
| 12 | 10 | 6 | 10.12 | 6.45 | 20.35 | 12.39 | 49.31 | 20347 |
| 13 | 5 | 1.5 | 0.76 | 0.92 | 1.01 | 0.53 | 3.22 | 2020 |
| 14 | 5 | 4 | 0.82 | 0.99 | 1.07 | 1.01 | 3.89 | 2140 |
| 15 | 2.5 | 1.5 | 0.18 | 0.23 | 0.22 | 0.21 | 0.84 | 880 |
| 16 | 2.5 | 4 | 0.21 | .027 | 0.27 | 1.01 | 1.76 | 1080 |

[1] Percentages correspond to GC area.
[2] Reaction performed with 100 psi propene.

EXAMPLE 6

Propenolysis of FAMEs

Various FAMEs were subjected to cross-metathesis with 1-propene using C827 according to the procedure described above. Canola FAME was the same as in example 1, Soy FAME was the same as in example 4, and Sun FAME was obtained from Nu-Chek-Prep and degassed by sparging with argon for 1 hour/L prior to being stored over activated alumina in a glove box under an argon atmosphere. The reactions were performed at 60 °C and under 130 psi of 1-propene using 5 ppm of catalyst. The results are provided in TABLE 7.

TABLE 7. Propenolysis of Various FAMEs[1]

| Entry | Seed Oil | Time (h) | $1C_{10}$ (%) | $2C_{11}$ (%) | 9DA (%) | 9UDA (%) | Yield (%) | $TON_{9DA}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Canola FAME | 2 | 10.53 | 7.59 | 16.75 | 11.39 | 46.26 | 33500 |
| 2 | Canola FAME | 4 | 10.42 | 7.56 | 16.93 | 11.47 | 46.38 | 33860 |
| 3 | Canola FAME | 2 | 10.9 | 7.64 | 16.97 | 11.38 | 46.89 | 33940 |
| 4 | Canola FAME | 4 | 11.09 | 7.85 | 17.82 | 11.85 | 48.61 | 35640 |
| 5 | SBO FAME | 2 | 0.77 | 0.98 | 0.98 | 0.94 | 3.67 | 1960 |
| 6 | SBO FAME | 4 | 0.72 | 0.95 | 0.96 | 0.92 | 3.55 | 1920 |
| 7 | Sun FAME | 2 | 0.51 | 0.61 | 0.56 | 0.61 | 2.29 | 1120 |
| 8 | Sun FAME | 4 | 0.5 | 0.6 | 0.55 | 0.62 | 2.27 | 1100 |
| 9 | Sun FAME | 2 | 3.1 | 3.21 | 3.3 | 3.16 | 12.77 | 6600 |
| 10 | Sun FAME | 4 | 2.79 | 3.02 | 3.21 | 3.14 | 12.16 | 6420 |

[1] Percentages correspond to GC area.

EXAMPLE 7

Propenolysis of FAMEs

The FAMEs used in Example 5 were subjected to cross-metathesis with 1-propene using C848 and C827 according to the procedure described above. The reactions were performed at 60 °C (unless specified otherwise) and under 130 psi of 1-propene for 4 hours using different catalyst loadings. The results are provided in TABLE 8.

TABLE 8. Propenolysis of FAMEs[1]

| Entry | Seed Oil | Catalyst (ppm) | $1C_{10}$ (%) | $2C_{11}$ (%) | 9DA (%) | 9UDA (%) | Yield (%) | $TON_{9DA}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Sun FAME | C827 (28) | 18.65 | 13.65 | 21.32 | 15.16 | 68.78 | 7614 |
| 2 | Canola FAME | C827 (18) | 13.19 | 9.63 | 20.78 | 14.91 | 58.51 | 11544 |
| 3 | Sun FAME | C827 (11) | 15.45 | 10.64 | 23.95 | 14.63 | 64.67 | 21773 |
| 4 | Canola FAME | C827 (7) | 13.41 | 8.69 | 20.72 | 13.48 | 56.3 | 29600 |
| 5[2] | SBO FAME | C848 (25) | 8.67 | 4.38 | 27.52 | 13.39 | 53.96 | 11008 |
| 6[2] | Canola FAME | C848 (18) | 15.19 | 9.65 | 25.74 | 15.68 | 66.26 | 14300 |

[1] Percentages correspond to GC areas.
[2] Reactions performed at 40 °C.

EXAMPLE 8

1-Butene Cross-metathesis reaction

Soy FAME, (Chemol, IF-24298) was flashed distilled under vacuum (< 1mm Hg). Degassed Soy FAME 7.5L (6.8 Kg, 22.9 mol) and 0.74 g (25 ppm/double bond) metathesis catalyst 827 were added to a 20L Parr Reactor and degassed with argon for 1 hr. 1-Butene was added while heating to 60°C, the pressure of the reaction was between 24 psi to 59 psi. The 1-butene was added using a one-way check valve to prevent back flow into the 1-butene cylinder.

After 4 hours, GC analysis indicated 10.5% 1-decene, 8.2% 3-dodecene, 19.6% methyl 9-decenoate and 14.6% methyl 3-dodecenoate. The pressure was released and vented into a fume hood. When the reactor was at ambient pressure, 50 ml of 1 M THMP solution in IPA (50 mol equivalents) was added, the reactor degassed with argon and heated to 60°C overnight (~18 hr).

The reactor was cooled to room temp and the contents were transferred to a 12 L flask with bottom out drain. The product was washed with 4 L of water and 4 L of brine. The washed metathesis product was dried over sodium sulfate, filtered and distilled under reduced pressure.

TABLE 9 lists the 4 main products from the vacuum distillation of butenolysis of Soy FAME.

TABLE 9. Products from the Cross Metathesis of 1-Butene and Soy FAME[1]

| Compound | GC Area Percent | Isolated Yields (g) |
|---|---|---|
| 1-Decene | 10.5% | 458.6 |
| 3-Dodecene | 8.2% | 475.1 |
| Methyl 9-Decenoate | 19.6% | 1494.5 [2] |
| Methyl 9-Dodecenoate | 14.6% | 1085.0 [3] |

[1] Metathesis Reaction #129-061 and Distillation Results #108-100

[2] Isolated 846.0 g of 96.9% purity and 648.5 g of 82.6% purity

[3] Isolated 989.8 g of 97.1% purity and 95.2 g of 64.3% purity

EXAMPLE 9

Butenolysis of Soy FAME

Soy FAME was reacted according to the general metathesis procedure provided above, using the catalysts identified below. 1-Butene was introduced in the reactor while the oil was cooled to 0 °C until about 3 equivalents of 1-butene/double bond of soy FAME were condensed. The reaction vessel was then sealed and the reaction mixture left at the indicated temperature for 4 hours before it was analyzed (the pressure inside the vessel would reach from about 30 psi to about 90 psi). The results are presented in TABLE 10.

TABLE 10. Butenolysis of Soy FAME using various catalysts.

| Entry | Catalyst | Loading (ppm/DB) | Temp. (°C) | 1-decene (%) | 3-dodecene (%) | $9C_{10}O_2Me$ (%) | $9C_{12}O_2Me$ (%) |
|---|---|---|---|---|---|---|---|
| 1 | 697 | 200 | 60 | 5.31 | 8.09 | 13.31 | 16.3 |
| 2 | 701 | 200 | 60 | 1 | 1.43 | 1.5 | 1.25 |
| 3 | 712 | 200 | 30 | 5.39 | 7.26 | 18.04 | 19.04 |
| 4 | 801 | 200 | 50 | 0.35 | 0.39 | 0.76 | 0.67 |
| 5 | 933 | 200 | 30 | 6.25 | 7.01 | 15.03 | 13.68 |
| 6 | 838 | 200 | 50 | 0 | 0.002 | 0.013 | 0.002 |
| 7 | 601 | 200 | 50 | 0.11 | 0.14 | 0.16 | 0.1 |
| 8 | 841-n | 200 | 60 | 3.27 | 4.69 | 5.24 | 5.2 |
| 9 | 727 | 200 | 30 | 0.65 | 4.93 | 1.12 | 2.74 |
| 10 | 831 | 200 | 30 | 6.98 | 6.54 | 17.8 | 15.22 |

Soy FAME was reacted according to the general metathesis procedure provided above, using the catalysts identified in the table. 1-Propene was introduced into the sealed, pre-cooled reactor held at the indicated temperature by a cooling bath. The reaction mixture was stirred at the indicated temperature for up to 40 hours. Samples were analyzed by GC analysis. The results are presented in Table 11.

TABLE 11. Low Temperature Propenolysis using Various 2nd Generation Grubbs Catalysts

| Exp# | Oil | α-olefin (XS) | Cat (ppm) | Temp °C | Time (h) | % 1C10 | %2C11 | %9DA | %9ul |
|---|---|---|---|---|---|---|---|---|---|
| 129-072 | SBO FAME | propene | C827(50) | 20° | 24 | 0 | 0 | 0 | 0 |
| 129-073 | " | " | C827(50) | 10° | 24 | 0 | 0 | 0 | 0 |
| 129-074 | " | " | C727(50) | 20° | 24 | 0 | 0 | 0 | 0 |
| 129-075 | " | " | C627(50) | 20° | 24 | 0 | 0 | 0 | 0 |
| 129-076 | " | " | C727(50) | 0° | 24 | 0 | 0 | 0 | 0 |
| 129-077 | " | " | C627(50) | 0° | 24 | 0 | 0 | 0 | 0 |
| 129-080 | " | " | C727(500) | 20° | 4 | 3.08 | 2.74 | 6.64 | 5.1 |
| 129-081 | " | " | C627(500) | 20° | 4 | 13.53 | 8.85 | 26.65 | 12.3 |
| 129-082 | " | " | C831(500) | 20° | 5 | 10.92 | 7 | 20.06 | 12.9 |
| 129-083 | " | " | C727(500) | 10° | 1.25 | 0.1 | 0.2 | 0.46 | 0.4 |
| 129-084 | " | " | C627(500) | 10° | 1.25 | 1.08 | 5.38 | 14.48 | 9.9 |
| 129-085 | " | " | C831(500) | 10 | 40 | 0.65 | 1.2 | 3.93 | 3.2 |
| 129-086 | " | " | C727(500) | 0° | 3.5 | 0 | 0 | 0 | 0 |
| 129-087 | " | " | C627(500) | 0° | 3.5 | 0 | 0 | 0 | 0 |
| 129-088 | " | " | C831(5000) | 0° | 4 | 11.16 | 8.19 | 18.27 | 13.4 |
| 129-089 | " | " | C627(5000) | 0° | 4 | 10.76 | 7.87 | 19.02 | 13.8 |

Other embodiments of this invention will be apparent to those skilled in the art upon consideration of this specification or from practice of the invention disclosed herein. Various omissions, modifications, and changes to the principles and embodiments described herein may be made by one skilled in the art without departing from the true scope and spirit of the invention which is indicated by the following claims. All patents, patent documents, and publications cited herein are hereby incorporated by reference as if individually incorporated.

**WHAT IS CLAIMED IS:**

1. A method of making a monounsaturated alkene composition comprising the steps of:

(a) providing a starting composition comprising one or more polyunsaturated fatty acids, polyunsaturated fatty esters, or carboxylate salts of polyunsaturated fatty acids;

(b) cross-metathesizing the starting composition with a short-chain olefin in the presence of a metathesis catalyst to form cross-metathesis products comprising: (i) one or more olefin compounds; and (ii) one or more acid-, ester-, or salt-functionalized monounsaturated alkenes; and

(c) separating at least a portion of one of the acid-, ester-, or salt-functionalized monofunctionalized alkenes from the cross-metathesis products to provide a monounsaturated alkene composition.

2. The method of claim 1, wherein the starting composition is a polyunsaturated fatty acid.

3. The method of claim 1, wherein the starting composition is a polyunsaturated fatty ester.

4. The method of claim 1, wherein the starting composition is a carboxylate salt of a polyunsaturated fatty acid.

5. The method of claim 1, wherein the starting composition comprises a polyunsaturated polyol ester.

6. The method of claim 1, wherein the starting composition comprises a $\Delta 9$ polyunsaturated fatty acid, a $\Delta 9$ polyunsaturated fatty ester, a carboxylate salt of a $\Delta 9$ polyunsaturated fatty acid, or a mixture thereof.

7. The method of claim 6, wherein the $\Delta 9$ polyunsaturated fatty acid comprises linoleic acid, linolenic acid, or a mixture thereof.

8. The method of claim 6, wherein the $\Delta 9$ polyunsaturated fatty ester comprises an alkyl ester of linoleic acid, an alkyl ester of linolenic acid, or a mixture thereof.

9. The method of claim 6, wherein the $\Delta 9$ polyunsaturated fatty ester comprises a vegetable oil.

10. The method of claim 9, wherein the vegetable oil comprises soybean oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, sunflower oil, canola oil, safflower

oil, palm oil, palm kernel oil, linseed oil, castor oil, olive oil, peanut oil, and mixtures thereof.

11. The method of claim 1, wherein the polyunsaturated fatty acid, ester, or carboxylate salt can be represented by the general formula:

$$CH_3\text{-}(CH_2)_{n1}\text{-}[\text{-}(CH_2)_{n3}\text{-}CH{=}CH\text{-}]_x\text{-}(CH_2)_{n2}\text{-}COOR$$

where:

R is hydrogen, an aliphatic group, or a metal ion;

n1 is an integer equal to or greater than 0;

n2 is an integer equal to or greater than 0;

n3 is an integer equal to or greater than 0; and

x is an integer equal to or greater than 2.

12. The method of claim 1, wherein the polyunsaturated ester is a polyol ester represented by the general formula:

$$R(O\text{-}Y)_m\,(OH)_n\,(O\text{-}X)_b$$

where

R is an organic group having a valency of (n+m+b);

m is an integer from 0 to (n+m+b-1), typically 0 to 2;

b is an integer from 1 to (n+m+b), typically 1 to 3;

n is an integer from 0 to (n+m+b-1), typically 0 to 2;

(n+m+b) is an integer that is 2 or greater;

X is $\text{–}(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$;

Y is –(O)C-R′;

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is an integer equal to or greater than 0;

n2 is an integer equal to or greater than 0;

n3 is an integer equal to or greater than 0; and

x is an integer equal to or greater than 2.

13. The method of claim 1, wherein the polyunsaturated ester is a polyol ester of glycerol that can be represented by the general formula:

$$CH_2A\text{-}CHB\text{-}CH_2C$$

where –A; –B; and –C are selected from

–OH;

$–O(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$; and

–O(O)C-R′;

with the proviso that at least one of –A, -B, or –C is

$–O(O)C\text{-}(CH_2)_{n2}\text{-}[\text{-}CH{=}CH\text{-}(CH_2)_{n3}\text{-}]_x\text{-}(CH_2)_{n1}\text{-}CH_3$.

In the above formula:

R′ is a straight or branched chain alkyl or alkenyl group;

n1 is an integer equal to or greater than 0;

n2 is an integer equal to or greater than 0;

n3 is an integer equal to or greater than 0; and

x is an integer equal to or greater than 2.

14. The method of claim 1, wherein the starting composition comprises at least 5% weight polyunsaturated compounds.

15. The method of claim 1, wherein the short-chain olefin has the structure:

$$R^7R^8C{=}CR^9R^{10}$$

where $R^7$, $R^8$ are each, independently, hydrogen or an organic group, with the proviso that at least one of $R^7$ or $R^8$ is an organic group.

16. The method of claim 15, wherein the short-chain olefin is a short-chain internal olefin.

17. The method of claim 16, wherein the short-chain internal olefin has the structure

$$R^7R^8C{=}CR^9R^{10}$$

where $R^7$, $R^8$, $R^9$, and $R^{10}$ are each, independently, hydrogen or an organic group, with the proviso that at least one of $R^7$ or $R^8$ is an organic group, and at least one of $R^9$ or $R^{10}$ is an organic group.

18. The method of claim 16, wherein the short-chain internal olefin is symmetric.

19. The method of claim 18, wherein the symmetric short-chain internal olefin has the structure:

$$R^7CH=CHR^9$$

where $R^7$ and $R^9$ are the same organic group.

20. The method of claim 19, wherein the symmetric short-chain internal olefin is selected from the group consisting of 2-butene, 3-hexene, and 4-octene.

21. The method of claim 16, wherein the short-chain internal olefin is asymmetric.

22. The method of claim 21, wherein the asymmetric short-chain internal olefin is selected from the group consisting of 2-pentene, 2-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 2-nonene, 3-nonene, and 4-nonene.

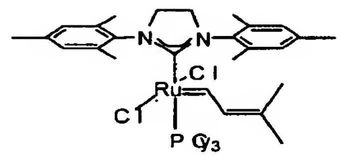
23. The method of claim 15, wherein the short-chain olefin is an α-olefin having the structure:

$$CH_2=CH\text{-}R^{10}$$

where $-R^{10}$ is an organic group.

24. The method of claim 23, wherein the α-olefin is selected from the group consisting of 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-nonene.

25. The method of claim 1, wherein the metathesis catalyst is selected from the group consisting of:



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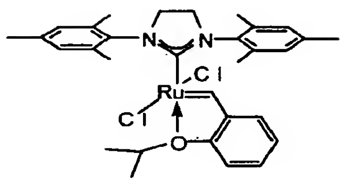

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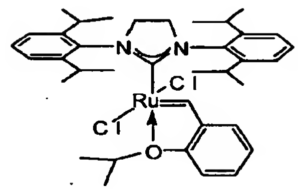

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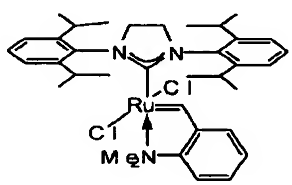

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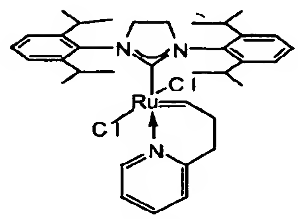

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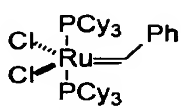

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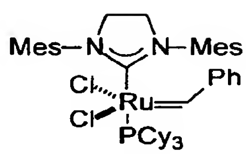

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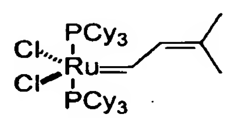

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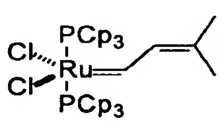

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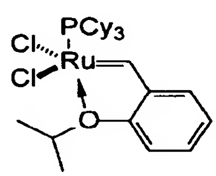

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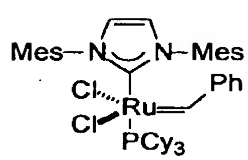

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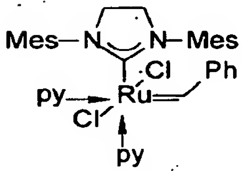

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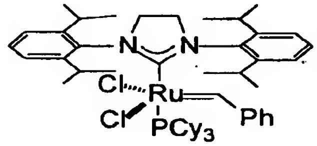

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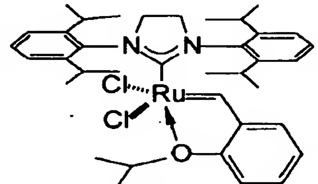

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where Ph is phenyl, Mes is mesityl, py is pyridine, Cp is cyclopentyl, and Cy is cyclohexyl.

26. The method of claim 1, wherein the separating step comprises distillation, reactive distillation, chromatography, fractional crystallization, membrane separation, liquid/liquid extraction, or a combination thereof.

27. The method of claim 1, wherein the monounsaturated alkene composition comprises

$$R^7R^8C{=}CH\text{-}(CH_2)_{n2}\text{-}COOR$$

where R is hydrogen, an aliphatic group, or a metal ion;

n2 is an integer equal to or greater than 0; and

$R^7$ and $R^8$ are each, independently, hydrogen or an organic group.

28. The method of claim 1, wherein the short-chain internal olefin is 2-butene and the monounsaturated alkene composition comprises

$$CH_3\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOR$$

where R is hydrogen, an aliphatic group, or a metal ion.

29. The method of claim 1, wherein the short-chain internal olefin is 3-hexene and the monounsaturated alkene composition comprises

$$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOR$$

where R is hydrogen, an aliphatic group, or a metal ion.

30. The method of claim 1, wherein the short-chain internal olefin is 1-propene and the monounsaturated alkene composition comprises a mixture of:

$CH_2{=}CH\text{-}(CH_2)_7\text{-}COOR$ and

$CH_3\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOR$

where R is independently hydrogen, an aliphatic group, or a metal ion.

31. The method of claim 1, wherein the short-chain internal olefin is 1-butene and the monounsaturated alkene composition comprises a mixture of:

$CH_2{=}CH\text{-}(CH_2)_7\text{-}COOR$ and

$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOR$

where R is independently hydrogen, an aliphatic group, or a metal ion.

32. The method of claim 1, wherein the monounsaturated alkene composition is at least 95% by weight pure.

33. The method of claim 1, wherein the monounsaturated alkene composition is at least 99% by weight pure.

34. A monounsaturated alkene composition made in accordance with the method of claim 1.

FIG. 1

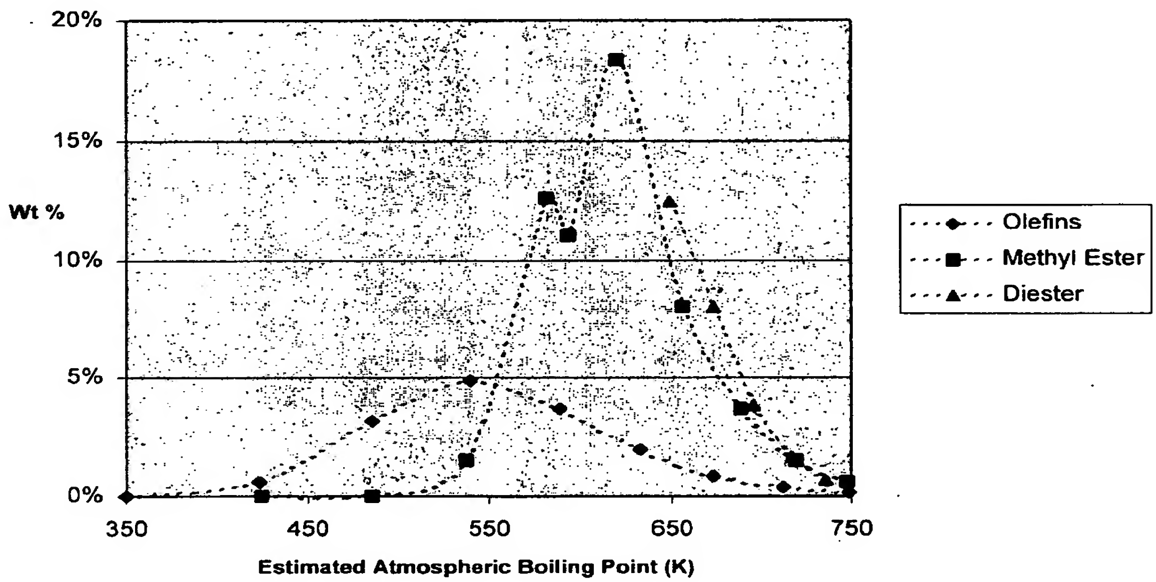
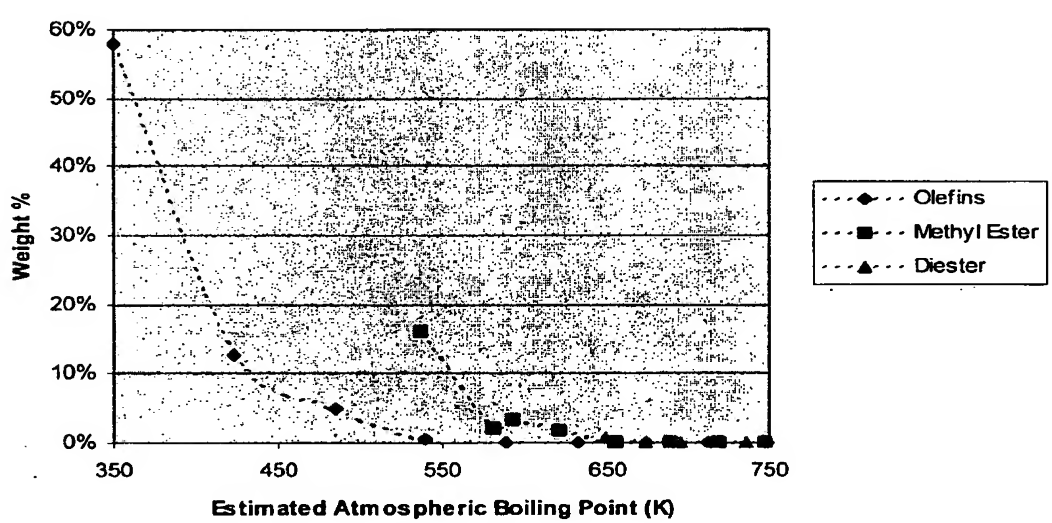

20%
15%
10%
5%
0%
Wt %
350
450
550
650
750
Estimated Atmospheric Boiling Point (K)
Olefins
Methyl Ester
Diester

FIG. 2


60%
50%
40%
30%
20%
10%
0%
Weight %
350
450
550
650
750
Estimated Atmospheric Boiling Point (K)
Olefins
Methyl Ester
Diester

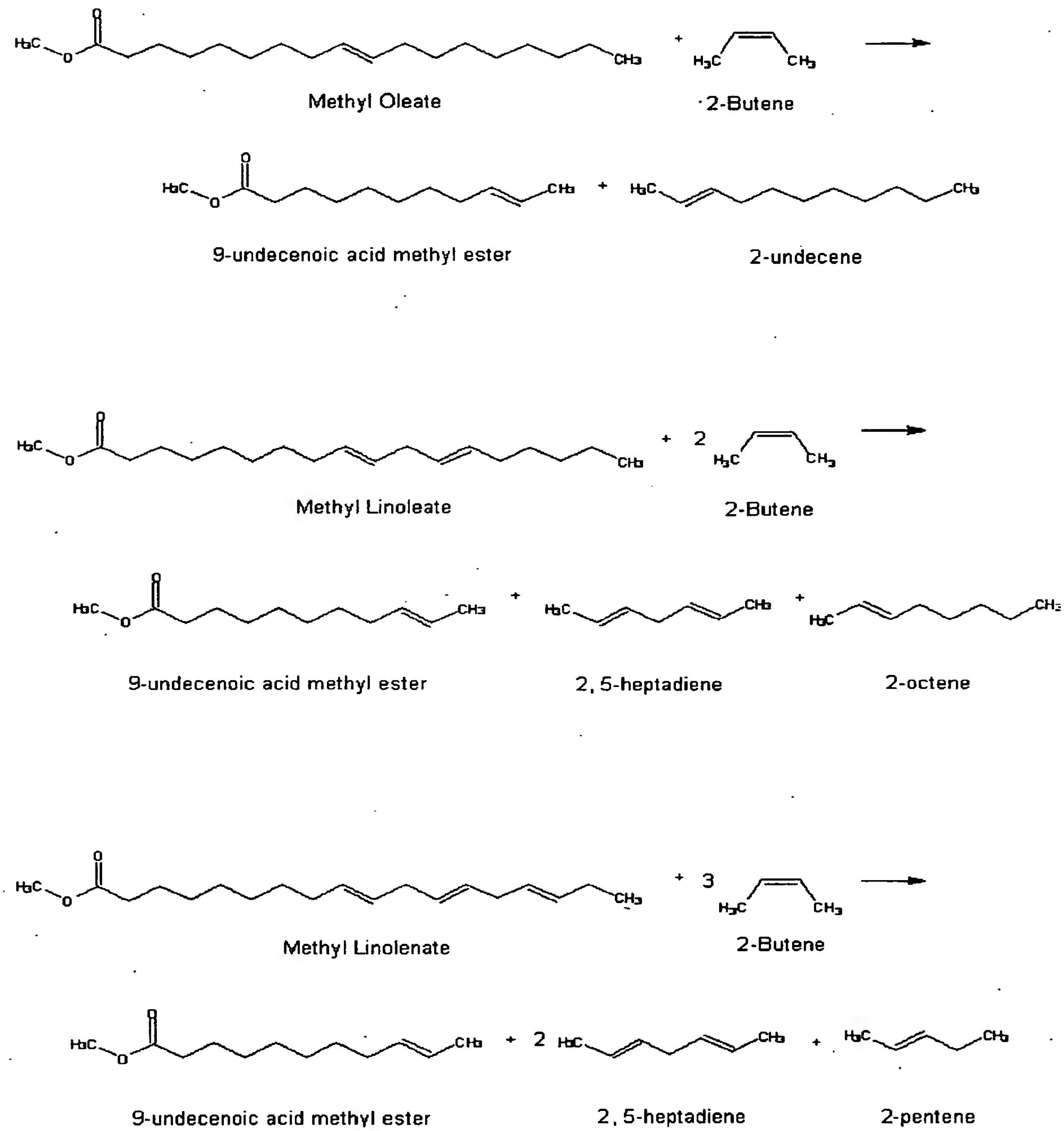

Methyl Oleate
2-Butene
9-undecenoic acid methyl ester
2-undecene
Methyl Linoleate
2-Butene
9-undecenoic acid methyl ester
2, 5-heptadiene
2-octene
Methyl Linolenate
2-Butene
9-undecenoic acid methyl ester
2, 5-heptadiene
2-pentene

**FIG. 3**

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2007/021939**

**A. CLASSIFICATION OF SUBJECT MATTER**

*C07C 11/02(2006.01)i, C07C 11/00(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 8 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
e-KIPASS, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
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| A | US 2005/0080301 A1 (The Dow Chemical Company Intellectual Property Section) 14 April 2005<br>See the whole document. | 1-34 |
| A | Ursula Biermann, et al. "New Syntheses with Oils and Fats as Renewable Raw Materials for the Chemical Industry." Angewandte Chemie International Edition, 2000, Vol. 39, 2206-2224.<br>See page 2211. | 1-34 |
| A | M. D. Refvik, et al. "Ruthenium-Catalyzed Metathesis of Vegetable Oils." Journal of the American Oil Chemical Society, 1999, Vol. 76, 93-98.<br>See the whole document. | 1-34 |
| A | Horst Baumann, et al. "Natural Fats and Oils - Renewable Raw Materials for the Chemical Industry." Angewandte Chemie International Edition in English, 1988, Vol. 27, 41-62.<br>See page 54.<br>--------------------------------------------End of documents-------------------------------------------------- | 1-34 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 18 FEBRUARY 2008 (18.02.2008) | **18 FEBRUARY 2008 (18.02.2008)** |

| Name and mailing address of the ISA/KR | Authorized officer |
|---|---|
| Korean Intellectual Property Office<br>Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea<br>Facsimile No. 82-42-472-7140 | KIM, Dong Seok<br>Telephone No. 82-42-481-8147 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
**PCT/US2007/021939**

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